



NASR-49(14)

May 26, 1965

Report No. 6

Quarterly Progress Report No. V February 1 to April 30, 1965

A STUDY OF BONDING BETWEEN GLASS AND PLASTIC
IN GLASS-REINFORCED PLASTICS: PHASE II

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SRI Project No. GCU-4525

FACILITY FORM 602

N65-86036
(ACCESSION NUMBER)

23
(PAGES)

CR 63714
(NASA CR OR TMX OR AD NUMBER)

(THRU)

None
(CODE)

(CATEGORY)

Prepared for

National Aeronautical and Space Administration
Washington 25, D.C.

Approved:

Adolph B. Amster for
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Copy No. _____

I INTRODUCTION AND SUMMARY

This report covers work done during the second quarter of Phase II of the project. In this phase we are studying methods for producing, on glass and silica fibers, an organic "finish" that will be bonded to the fibers by silicon-carbon bonds.

Considerable effort was devoted during this quarter to physical methods for evaluating surface treatment of low specific surface materials. The physical methods appear to offer the best, if not the only, satisfactory way of measuring changes wrought by surface treatment of end-use materials. Conventional methods of analysis (e.g., infrared spectroscopy and classical analytical methods) which are effective for high specific surface materials, are of little or no use for materials which have a low surface-to-weight ratio such as glass plates, cylinders, and even coarsely ground glass.

Alkoxylation was investigated as an alternative and more desirable route -- than chlorination or fluorination -- to reactive intermediate surface groups on silica and glass. Work also was continued with finely divided materials of high specific surface. Application of chlorination and alkylation reactions was extended to low specific surface materials, namely glass microscope slides, and silica and glass rings. A sonic method for the study of bonding between plastic and surface-modified glass was evaluated and found to be inadequate.

Samples have been prepared for dilatometric measurement of adhesion in a glass-plastic composite system. A peel test apparatus was designed and constructed, and a preliminary evaluation of the apparatus with unmodified glass and silica rings was accomplished. The effect of surface treatment upon the angle of contact between glass plates and selected polar and non-polar liquids was demonstrated.

II DISCUSSION

Materials

While silica in various forms was used earlier in this project to develop chlorination, fluorination, and alkylation procedures, our current work calls for extending surface treatment methods to glass, which contains a variety of ionic species. A glass powder (of unknown composition, supplied by Fisher Scientific Co.) has been used for initial experiments. Attempts to correlate surface "population" of chloride atoms with surface area, as measured by adsorption of nitrogen, were unsuccessful. The difficulty appears to lie in the change in measured surface area with change in the temperature of initial desorption. This effect may be attributed to the presence of fractures in the glass particles. These fractures may be completely filled with adsorbed gases at ambient temperatures, and at higher temperatures gases may be desorbed from these fractures; the result is higher measured surface areas, as shown in Table I. Chlorination at 500°C or fluorination at 200°C may cause an unknown amount of desorption and an equally unknown increase in the halogenated surface area. Therefore quantitative correlation between measured surface area and the concentration of surface groups cannot be made.

Attempts to obtain fire-polished glass beads of comparable specific surface were unsatisfactory. Although Superbrite (Minnesota Mining and Manufacturing Company) spherical glass beads in diameters as small as 29 microns are available, these beads are of a soda-lime composition and leach severely in water. Consequently, the Fisher Scientific glass powder will be used until such time as quantitative correlations between surface area and concentration of reactive groups is necessary.

Chlorination

Chlorination reactions proceeded smoothly on finely divided materials. A modified reactor, shown in Fig. 1, was very effective; with a silica tube it may be operated to 1000°C in a tube furnace. The effect of temperature upon the chlorination of low-iron silica with phosgene is shown in Table II. The data at 500°C and higher agree well with previous results. The erratic results at 335 and 400°C may be explained by the observed variability of surface area with desorption temperature. Thus, at higher temperatures, the rate of desorption (and of increase in surface area) may be rapid and reproducible, while at lower temperatures, the rate may be much slower, and much less reproducible. The problem of accurate measurement of surface area of ground glass particles will be avoided in the future, if possible.

Chlorination of glass and silica rings was accomplished in the apparatus shown in Fig. 2. However, difficulties arose in maintaining a 500° temperature at the surface of the inner jacket. These difficulties must be overcome before the apparatus can be useful for chlorination of glass rings with phosgene.

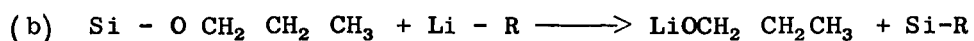
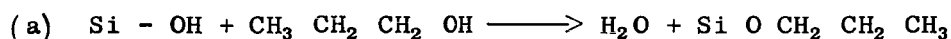
Fluorination

Fluorination of rings for peel tests was conducted at 200°C in the apparatus shown in Fig. 2. No problems were encountered in heating to 200°C.

Fluorination of microscope slides for contact angle studies was carried out in apparatus described previously. The presence of metallic ions, or other differences between glass and silica, resulted in an interesting temperature effect: Fluorination at low temperatures, ca. 100°C, resulted in severe and non-uniform etching of the surface; at 150°C, a clear surface was obtained, but a thin, transparent film of nonvolatile metal fluorides could be peeled from the glass surface. Optimum conditions for this reaction have not yet been found.

Alkoxylation

Alkoxylation of surface-based SiOH groups offers an alternative to chlorination or fluorination as a route to reactive surface groups. This reaction was carried out on glass powder and microscope slides using n-propyl alcohol, according to the method of Iler.¹ Analyses on the powdered glass are not complete, but the properties of the product indicate the reaction was successful. Alkoxylation offers advantages of lower temperature, fewer possible side effects (such as etching), and greater safety of operation as compared to fluorination or chlorination:



Alkylation

The alkylation of chlorinated, fluorinated, or alkoxyated materials was accomplished in a straightforward fashion with the appropriate organolithium compound. In the case of glass rings for peel tests, the halogenation apparatus (Fig. 2) was flushed with nitrogen, the inner jacket was quickly removed and immersed in a solution of the organolithium compound. After alkylation, the tube was carefully cut into 1.5 inch lengths.

Adhesion Evaluation

Final evaluation of the effect of surface modification of glass fibers must be done on a finished laminate, or other end-use product. However, experiments on suitable model systems provide a less expensive and much more rapid screening procedure. To this end, four methods for studying the effect of surface treatment upon surface properties were examined: sonic, dilatometric, peel tests, and contact angle measurement. These

¹R. K. Iler, Method of Esterifying the Surface of a Silica Substrate Having a Reactive Silanol Surface, and Product Thereof, U.S. Pat. No. 2,657,149 (Oct. 1953).

methods become somewhat more important in the absence of analytical data concerning the surface concentration of modifying groups.

Sonic Method

The sonic method for evaluation of bonding has been successfully employed in a variety of circumstances. The possibility that the method could be adapted to at least the qualitative measurement of bonding between a finely divided filler and a polymeric matrix was explored. The method depends upon the absorption of sound waves at the interfaces between phases of a composite material. The apparatus used was a barium titanate transducer placed upon a "button" of glass powder-filled elastomer 7.5 mm thick and 25 mm O.D. General Electric RTV-615 silicone polymer was used for the elastomer, because of its ease of formulation and fabrication. Buttons were fabricated with 50% (by weight) of glass powder.

The sonic method, as used, was unsatisfactory, due to the poor reproducibility of results from sample to sample, and between successive measurements upon the same sample. Effort in this direction was discontinued.

Dilatometric Method

Six samples of a 1:1 mixture of glass and RTV-615 silicone elastomer are ready for evaluation on the dilatometric apparatus. These, and others, will be run when the instrument becomes available. This instrument, which belongs to the U.S. Air Force is being used extensively in the evaluation of solid propellant formulations. It will be made available for use, without fee, on this contract.

Peel Tests

Peel tests were carried out on the apparatus shown in Fig. 3. Details of its construction and operation are given in the figure, and in the Experimental section. Table III summarizes the data to date. These data were obtained with a Baldwin-Tate-Emery load tester. The glass or silica rings were wrapped with 0.75- inch wide commercial Scotch tape, using a constant and reproducible 12-pound load. The wrapped rings were conditioned in a constant humidity chamber. The temperature and humidity in this chamber approached, but did not quite meet the $73 \pm 2^{\circ}\text{F}$ and the $51 \pm 2\%$ relative humidity called for in ASTM standards.² Room temperature at night dropped so low that the heater was inadequate for a period of 4-6 hours. More precise control will be exercised when precise data are required.

Table III gives data from five separate runs on each of nine rings. The first seven rings were silica, the last two Pyrex glass. The Baldwin tester was not equipped with a recorder and, because of the rapid pull rate, no attempt was made to obtain more than the high and low readings. The high value is much more significant than the low value, for the low reading on the tester could be, consistently, correlated with visible regions of poor bonding. The last column in the table shows the peel force in pounds per inch of tape width, for the average of the high and low values.

These peel tests were made to gain experience in wrapping rings and operating the equipment, and to collect data on untreated rings for reference. A general improvement in the quality of the data for the last two runs is evident, especially in the low values. This resulted, almost surely from improved wrapping technique.

²1964 Book of ASTM Standards, Part 16, Structural Sandwich Constructions; Wood; Adhesives, American Society for Testing Materials, Philadelphia, 1964.

- a. ASTM Peel Test D903-49
- b. ASTM Climbing Drum Peel Test D1781-62.

Variations from low to high values for a particular ring do not exceed 9%, which may be considered good for the method in its present state of development.

Contact Angle Measurements

Contact angle measurements, of a preliminary nature, were made using water on microscope slides which had been fluorinated and washed with water, and on slides that had been cleaned by the more conventional acid-dichromate method. All fluorinated slides showed contact angles of 5-10°, while the acid-cleaned slides showed variable angles, from 5° to 46°. Thus, it would appear that fluorination and hydrolysis is the more reliable of the two cleaning methods. The finite contact angles, * instead of zero, obtained on cleaned slides were ascribed to contamination by adsorption from air during the period between cleaning and measurement.

III EXPERIMENTAL

Materials

As reported in the last quarterly report, the surface area of commercial low-iron silica could not be exactly ascertained by the method of nitrogen adsorption, because the measured surface area increased as the temperature of initial desorption increased. This effect was attributed to fractures in the particles possibly caused by grinding or rough handling. Therefore, a search was made for a source of fire-polished glass beads. The microbeads marketed by 3M were unsatisfactory due to their high content of alkali metals, and the high pH of water suspensions.

From several other sources for glass beads, all samples (2-4 mm OD) were very pitted (and probably fractured) due to rough handling, or other causes. One grade of Pyrex glass bead was found that was smooth and polished, but its 6 mm O.D. was too large to be useful. Therefore, the original supplies of low-iron silica and ground glass (Fisher, 200 mesh

glass powder), were used. The latter is presumed to be a soft glass. It was cleaned and sized by washing with a stream of tap water on a 325 mesh Tyler screen to remove finer particles. The portion retained on the screen (200-325 mesh) was then washed with several portions of distilled water, the water decanted, the glass washed with three portions of reagent grade dioxane, then with three portions of reagent grade low-boiling petroleum ether, and finally the glass powder was dried on a rotating evaporator at 35-40°C and a pressure of 1 mm mercury. This material was used for all work with glass powder. The maximum surface area, calculated on the assumption that all particles were spherical and of 325 mesh (0.0043 cm) diameter, was 0.053 meters²/gram. The observed surface area, from a nitrogen flow-measurement, was 0.11 meters²/gram, when the initial desorption temperature was 155°C. The results of surface area measurements as a function of desorption temperature are shown in Table I.

Chlorination

Chlorination of particulate glass and silica was accomplished with phosgene in the reactor shown in Fig. 1. The effect of temperature of halogenation upon the chloride content of product is shown in Table II. The low values for surface chloride concentrations obtained at high temperatures (600°C-800°C) may be attributed to the more rapid disproportionation of intermediate surface-based structures to silicon tetrachloride and oxides of silicon. These values are in agreement with those obtained in Phase I of this work. The excellent agreement between the two values at 500°C may be somewhat fortuitous, although reproducibility of results at 500°C and higher is good. The large variation in results at temperatures below 500°C may be attributed, at least in part, to the effect of desorption temperature upon the effective surface area of the sample, as shown in Table I.

Chlorination of glass and silica rings (for peel test evaluation) was carried out at 500°C in the apparatus shown in Fig. 2. Chlorination in this apparatus was discontinued due to difficulties of heating the inner (sample) jacket. The well in the inner jacket was heated with a silica-sheathed immersion heater surrounded with 80 mesh alumina. The heating element failed after one run because of the high filament temperature required to maintain 500°C at the surface of the jacket.

After chlorination, the system was flushed with dry nitrogen and the inner jacket removed for further treatment. Finally the treated glass tube was carefully cut into cylinders (or sleeves), 1.25 inch long, for use in peel tests.

Fluorination

Fluorination of rings for peel tests was carried out with elemental fluorine at 200°C, in the apparatus shown in Fig. 2, using sodium chloride as a heat-transfer agent around a Calrod heater.

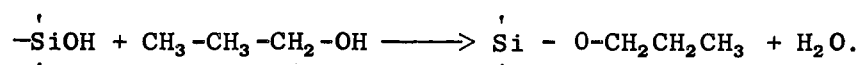
Fluorination of standard microscope slides was carried out in the apparatus shown in Fig. 2 of the Summary Technical Report (July 1964). Whereas the fluorination of silica (which produces volatile products exclusively) was smooth, the fluorination of glass was complicated by the formation of nonvolatile fluorides. At low temperatures deep etch lines approximately perpendicular to the four edges of the plate were formed. Examination under a microscope revealed that they probably were initiated at notches, resulting from the cutting operation, along the edges of the glass slides.

Fluorination of glass microscope slides at 150°C for 0.25 hour produced a transparent surface that was not etched with lines, but which was covered with a thin transparent layer of metal fluorides. This film was easily peeled from the glass substrate. Its thickness was governed

by the length of time of exposure to fluorine gas. Control of time and temperature of fluorination resulted in unmarred fluorinated surfaces. Optimum conditions have not been established for this reaction. These plates were used for contact angle measurements.

Alkoxylation

Alkoxylation of surface-based SiOH groups on glass was accomplished according to the reaction



The reaction was carried out at 180°C with n-propyl alcohol, in a pressure vessel, as recommended by Iler.¹ Glass powder and glass microscope slides were alkoxyated for subsequent use.

Alkylation

Alkylation of glass and silica samples was accomplished by causing the appropriate chlorinated, fluorinated, or alkoxyated sample to react with the desired organolithium compound. n-Butyllithium was prepared from n-butyl bromide and lithium metal, or was purchased from a commercial supplier. Other organolithium compounds were prepared by exchange between the appropriate organic halide and n-butyllithium.

Adhesion Evaluation

Sonic Method

Samples were prepared by casting buttons in metal planchets 7.5 mm deep and 25 mm diameter. The buttons were cast from a 1:1 mixture of glass and RTV-615 Silicone (General Electric Co.) polymer. The mixture was degassed and poured in a chamber at reduced pressure, in order to obtain bubble-free castings. Attempts to prepare methyl acrylate and methyl acrylate-butyl acrylate copolymer rubbers for this purpose gave unsatisfactory products.

Sonic testing of these samples were carried out with the assistance of the Sonics Department of the Institute's Physics Division. A barium titanate transducer served as a source, and as a receiver for the sonic energy not absorbed by the sample. The method, based upon the absorption of energy by nonhomogeneous materials, was discarded because of poor reproducibility of readings from duplicate samples.

Dilatometric Method

Samples were prepared from a 1:1 glass:RTV Silicone 615 rubber composite, cast in a bar 0.5 x 0.5 x 3.0 inches. Aluminum tabs were cast on each end to adapt to the extensometer rig.

Six samples of untreated glass are now ready for testing.

Peel Tests

The apparatus for carrying out peel tests is shown in Fig. 3. It was designed to evaluate the effect of surface modification of glass adherends upon the peel strength of pressure-sensitive tapes.

The roller-stirrup design was chosen for simplicity of construction, reproducibility of operation and ease of surface preparation of cylindrical samples. The preparation of samples may, in some cases, be more time-consuming than other peel test methods.² Particular advantages of this method for peel testing are: the apparatus is self-aligning; the angle of peel is always (essentially) 90°; and the configuration of the cylindrical glass adherend is such that it is readily halogenated and alkylated.

Glass cylinders, after treatment, were wound with tape as follows: a suitable length of tape was placed, adhesive side up, on a smooth flat surface which was cushioned with a smooth sheet of rubber; the glass

ring to be tested was slipped on the aluminum roller; the roller was centered on the tape, the leading edge of the tape fixed to the roller, and the tape wound by pushing the roller over the tape. Uniformity in winding was achieved by providing a device to keep the tape under constant tension, and by providing a guide and a 12-pound weight for the roller.

Small variations in the inside diameter of the glass rings were accommodated by wrapping the roller with one or more turns of a cloth-backed adhesive tape.

Peel-test rings and tape were conditioned in a constant temperature, constant humidity chamber. The chamber was a plastic dry box fitted with a thermostat, heater, and blower. A constant relative humidity of 51% (at 73°F) was maintained with a large shallow tray of saturated calcium nitrate solution. Relative humidity and temperature were recorded with a Bendix Hygro-Thermograph.

Contact Angle Measurements

Contact angle measurements were conducted by the Institute's Metallurgy Department. To date, only preliminary measurements have been made to evaluate the effectiveness of cleaning methods.

Contact angle measurements were made on glass microscope slides (Erie Scientific Co. No. 2950). A small drop of water was placed on the slide from a fine glass capillary tube. The drop was photographed through a microscope and prism arrangement to obtain an enlargement of ca. 35X. The angle of contact was then measured on the photograph with a rule and protractor.

Plates which were cleaned by fluorination and subsequent hydrolysis with distilled water showed consistently low contact angles of 5-10°.

(Contact angles greater than, but near, zero for clean glass surfaces were tentatively ascribed to atmospheric contamination during exposure prior to measurement.)

Glass slides which had been cleaned in freshly prepared sulfuric acid-dichromate solution exhibited irregular wetting, with values as high as 46° .

IV FUTURE WORK

E-glass fibers will be used as a high specific-surface material for chlorination and alkoxylation studies.

Alkoxylation will be fully evaluated as an alternative to chlorination or fluorination for the production of reactive intermediate groups on glass surfaces.

Alkylated and arylated glass, both of high and low specific surface will be prepared for adhesion evaluation.

Adhesion evaluation will be done on samples for dilatometry and peel testing. Contact angle measurements will be used as a guide in choosing methods of surface treatment.

ACKNOWLEDGMENTS

Mrs. Fern Jantzeff carried out the alkoxylation studies on ground glass and the preparation and evaluation of samples for sonic and dilatometric studies. Mr. Michael Bertolucci carried out fluorination and chlorination reactions and the preparation and evaluation of peel test samples. Mr. J. A. Rinde of the Propulsion Sciences Department was consultant for the dilatometric work; Mr. John Martner of the Sonics Department was consultant for the sonic testing work; Mr. John Saunders

of the Metallurgy Department conducted contact angle measurements and
Dr. Harold Eding carried out surface area measurements.

Respectfully submitted,

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DLC:aeb

Table I

The Effect of Initial Degassing Temperature
on Surface Area
as Measured by Nitrogen Adsorption

Notebook Reference	Material	Surface Area (Meters ² per Gram)	
		Calculated from Particle Size	Measured by N ₂ Adsorption following Desorption at the Indicated Temperature
7452-25	Powdered Glass		240°C - 0.04
			335° - 0.10
7452-25	Low-Iron Silica		160° - 0.04
			200° - 0.06
			260° - 0.07
			335° - 0.08
7452-69	Powdered Glass	0.053*	155° - 0.11

*Calculated on the basis of spherical particles of the minimum size
(4.3×10^{-3} cm) retained by a 325 mesh screen.

Table II

The Effect of Temperature Upon the
Chlorination of Low-Iron Silica with Phosgene

Notebook Reference	Temperature °C	Chloride Concentration (mg Cl/g SiO ₂)
7452-20	800	0.0021
-17	700	0.0054
-16	600	0.0060
-15	500	0.077
-22	500	0.077
-24A	400	0.016
-24B	400	0.024
-26	400	0.010
-27A	335	0.020
-27B	335	0.015

Table III
Summary of Peel Test Data ⁽¹⁾

Notebook Reference	Ring No. (and type)	Cleaning Procedure	Conditioning Period		Peel Data ⁽³⁾		
			Before Wrap (hrs)	After Wrap (hrs)	lbs. for 0.75 in. wide tape		Lbs/in. (Avg)
					Low	High	
7452-70	1 (silica)	(4)	17	24	1.01	1.07	1.39
	2 (silica)	(4)	17	24	1.00	1.06	1.34
	3 (silica)	(4)	17	24	1.09	1.13	1.48
	4 (silica)	(4)	17	24	1.05	1.11	1.44
	5 (silica)	(4)	17	24	1.06	1.11	1.45
	6 (silica)	(4)	17	24	1.06	1.12	1.45
	8 (silica)	(4)	17	24	1.10	1.13	1.49
	9 (Pyrex)	(4)	17	24	1.40	1.45	1.89
	10 (Pyrex)	(4)	17	24	1.30	1.42	1.81
7452-73	1 (silica)	(4)	2 $\frac{1}{2}$	24	0.90	0.96	1.24
	2 (silica)	(4)	2 $\frac{1}{2}$	24	0.85	0.92	1.18
	3 (silica)	(4)	2 $\frac{1}{2}$	24	0.92	0.98	1.27
	4 (silica)	(4)	2 $\frac{1}{2}$	24	0.88	0.94	1.21
	5 (silica)	(4)	2 $\frac{1}{2}$	24	0.85	0.91	1.17
	6 (silica)	(4)	2 $\frac{1}{2}$	24	0.91	0.97	1.25
	8 (silica)	(4)	2 $\frac{1}{2}$	24	0.94	0.97	1.27
	9 (Pyrex)	(4)	2 $\frac{1}{2}$	24	0.85	0.90	1.17
	10 (Pyrex)	(4)	2 $\frac{1}{2}$	24	0.85	0.90	1.17
7452-80	1 (silica)	(5)	24	25	0.95	1.00	1.30
	2 (silica)	(5)	24	25	0.92	0.97	1.26
	3 (silica)	(5)	24	25	0.94	0.98	1.28
	4 (silica)	(5)	24	25	0.91	0.95	1.24
	5 (silica)	(5)	24	25	0.95	1.00	1.30
	6 (silica)	(5)	24	25	-	-	-
	8 (silica)	(5)	24	25	0.96	0.97	1.28
	9 (Pyrex)	(5)	24	25	0.83	0.90	1.15
	10 (Pyrex)	(5)	24	25	0.86	0.92	1.17
7452-87	1 (silica)	(4)	25	66	1.12	1.15	1.52
	2 (silica)	(4)	25	66	1.10	1.15	1.50
	3 (silica)	(4)	25	66	1.07	1.12	1.46
	4 (silica)	(4)	25	66	1.10	1.13	1.48
	5 (silica)	(4)	25	66	1.10	1.14	1.49
	6 (silica)	(4)	25	66	1.07	1.11	1.45
	8 (silica)	(4)	25	66	1.06	1.10	1.44
	9 (Pyrex)	(4)	25	66	1.00	1.05	1.37
	10 (Pyrex)	(4)	25	66	1.01	1.07	1.39
7452-90	1 (silica)	(4)	17	24	0.99	1.03	1.35
	2 (silica)	(4)	17	24	0.98	1.03	1.34
	3 (silica)	(4)	17	24	0.99	1.04	1.35
	4 (silica)	(4)	17	24	0.97	1.02	1.33
	5 (silica)	(4)	17	24	0.96	1.00	1.31
	6 (silica)	(4)	17	24	0.94	0.99	1.29
	8 (silica)	(4)	17	24	0.96	1.00	1.31
	9 (Pyrex)	(4)	17	24	0.90	0.95	1.23
	10 (Pyrex)	(4)	17	24	0.90	0.98	1.25

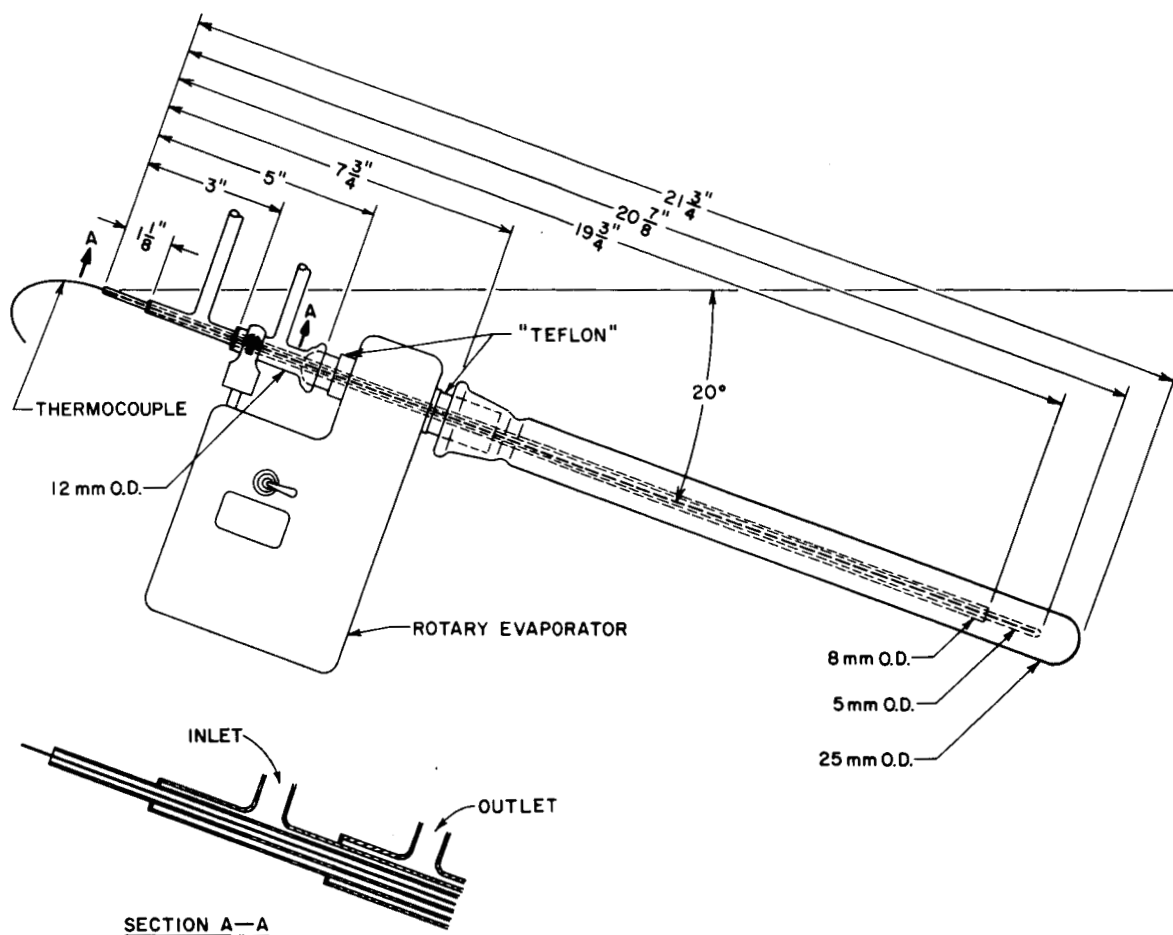
¹These data were obtained on a Baldwin-Tate-Emery Testing machine, at the rate of 6 inches per minute, using the 6 lb full-scale range.

²All operations were carried out in a plastic environmental chamber at control points of $51 \pm 2^\circ$ R.H. and $73 \pm 2^\circ$ F. Control of temperature was good except for the cooler portion of the night when the heater was inadequate to prevent a temperature drop (and consequent change in R.H.) of $5-10^\circ$.

³The Baldwin-Tester was not recording. Only high and low values are given here. Low values were easily associated with an area of poor control between tape and ring.

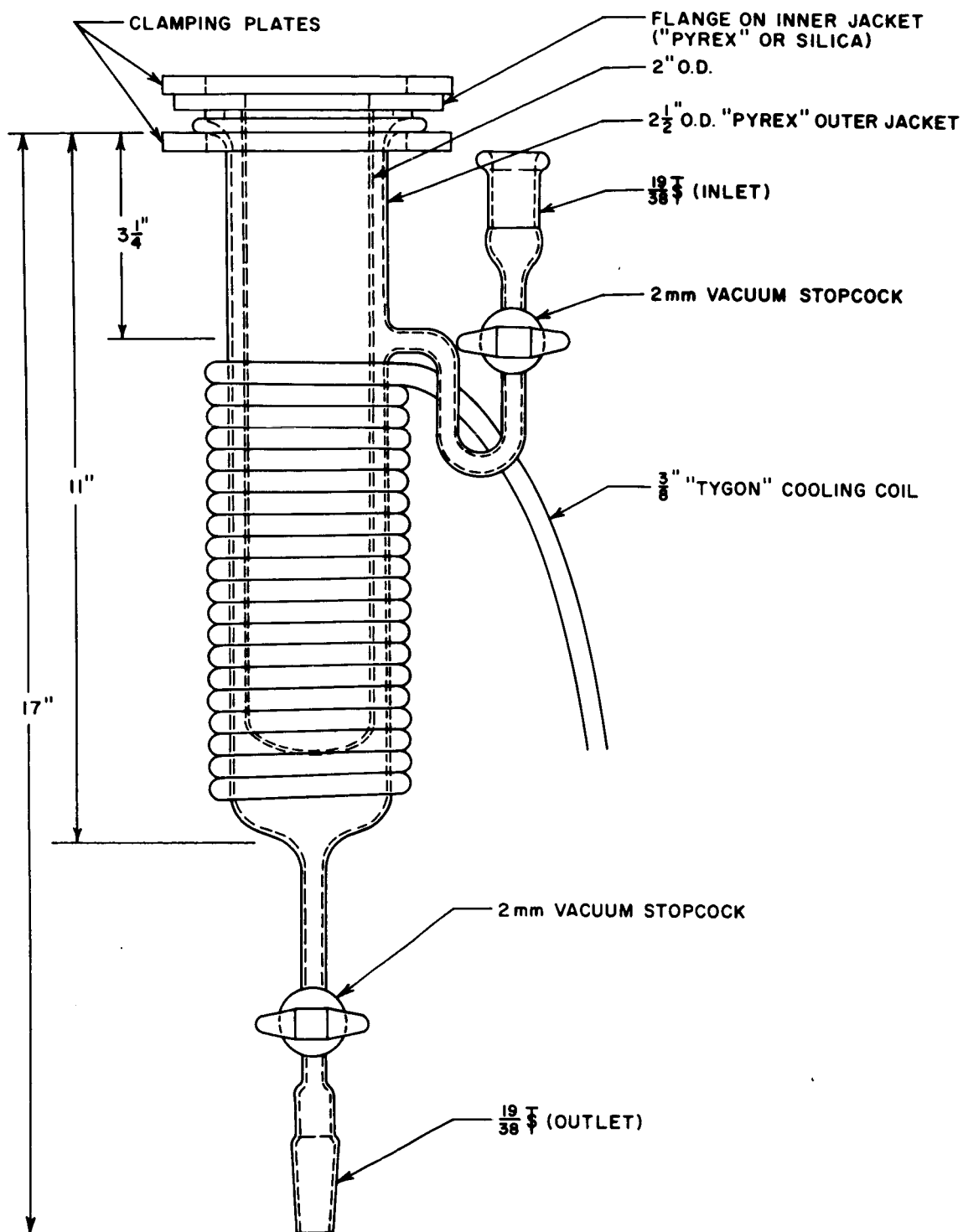
⁴Rings were cleaned by wiping with toluene, drying, soaking two hours in fresh dichromate-sulfuric acid solution, thoroughly washing with distilled water, and drying at 200° C.

⁵Rings were cleaned by wiping with toluene, soaking in clean dichromate-sulfuric acid for 65 hours, thoroughly washing, and drying at 200° C.



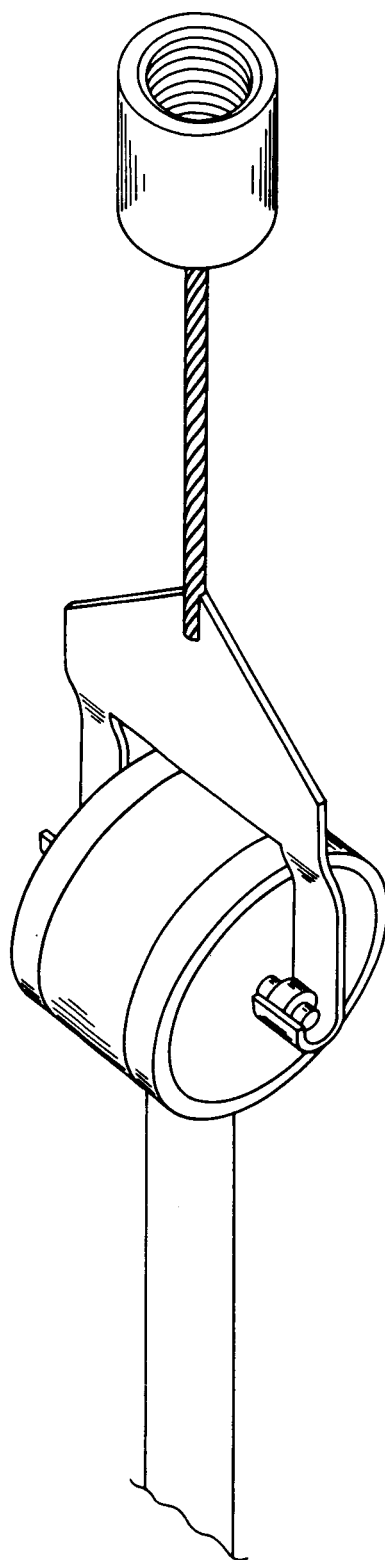
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FIG. 1 APPARATUS FOR HALOGENATION OF PARTICULATE MATERIALS



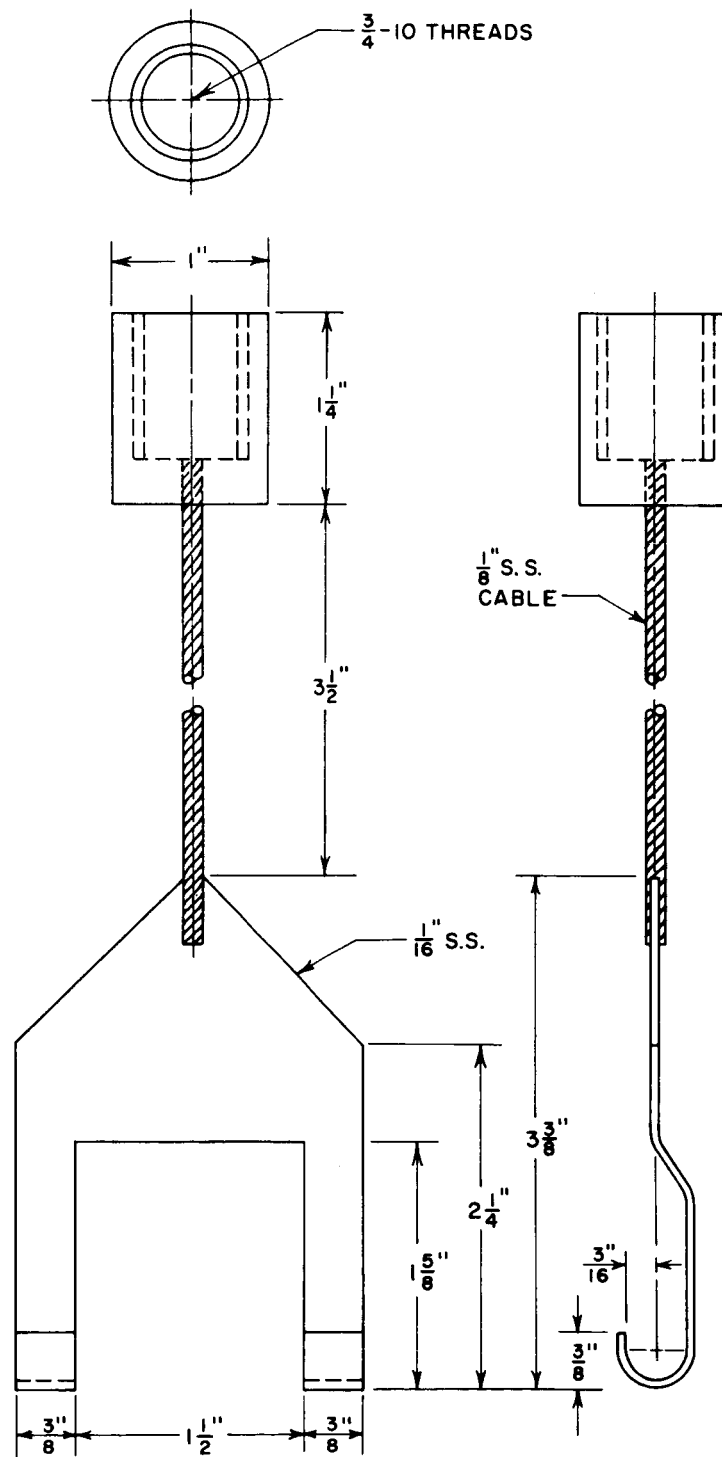
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FIG. 2 APPARATUS FOR HALOGENATION OF RINGS FOR PEEL TESTS



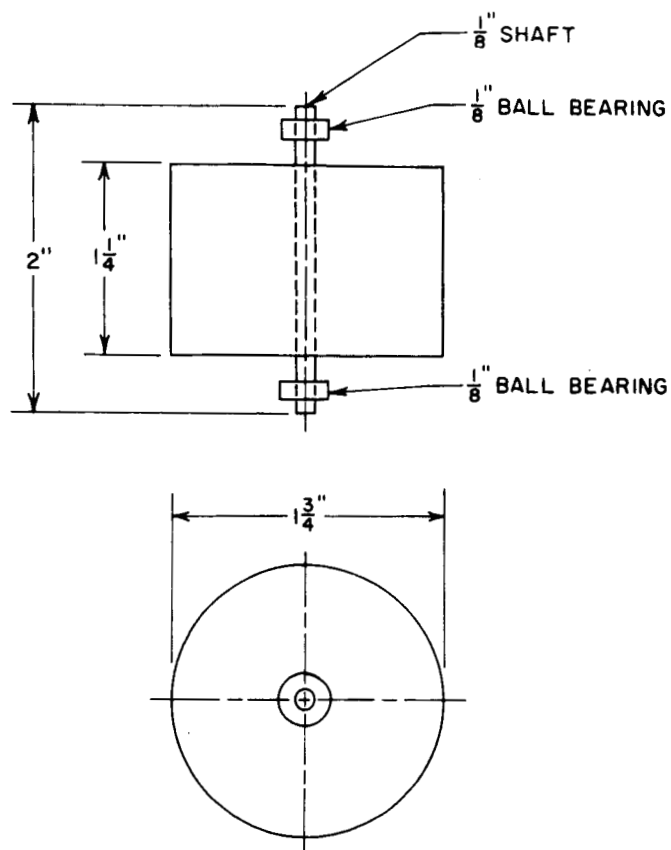
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FIG. 3(a) APPARATUS FOR PEEL TEST



TB-4525-1

FIG. 3(b) APPARATUS FOR PEEL TEST — DETAIL OF STIRRUP CONSTRUCTION



TA-4525-2

FIG. 3(c) APPARATUS FOR PEEL TEST — DETAIL OF ROLLER CONSTRUCTION